Syntheses, X-ray structures and characterisation of luminescent chromium(III) complexes incorporating 8-quinolinato ligands

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Abstract

A series of six coordinate homoleptic and heteroleptic Cr(III) complexes have been formed that incorporate 8-quinolinato ligands. Three classes of complex have been synthesised and characterised: (i) $[Cr(Q)_3]$; (ii) $[Cr(Q)_2(H_2O)_2]Cl$; (iii) $[Cr(Q)(N\hat{}N)_2](PF_6)_2$ (where Q is a ligand, 8-hydroxyquinoline, 8-hydroxy-2-methyl-quinoline, or 8-hydroxy-5-nitroquinoline; N^N = 1,10-phenanthroline or 2,2'-bipyridine). Single crystal X-ray structures were obtained for four complexes giving examples of $[Cr(Q)_2(H_2O)_2]Cl$, two $[Cr(Q)(bipy)_2](PF_6)_2$ and $[Cr(Q)(phen)_2](PF_6)_2$. Each complex shows the ligands in the expected coordination mode with a distorted octahedral geometry evident at the metal centre. The UV-vis. absorption data allowed assignments of the quinolinato-centred electronic transitions together with a much weaker spin allowed *d-d* transition ($^4A_2 \rightarrow {}^4T_2$) around 550 nm. Each complex was found to be luminescent in aerated MeCN solution at room temperature, which was attributed to a ligand-centred fluorescence based on the coordinated quinolinato ligand.

Introduction

Coordination complexes of Cr(III) continue to stimulate interest and investigation. In particular, the electronic properties of octahedral complexes of Cr(III) have been investigated in a number of contexts, including luminescence, photoredox catalysis, and solar cells.[1] In fact the photophysics and photochemistry of polypyridyl complexes of Cr(III) has been known for several decades[2] and continues to drive interest in these compounds. A detailed understanding of the excited state electronic configurations (particularly the ordering of the $^4T_2$ and $^2E/^2T_1$ excited states) of Cr(III) can allow the design of complexes for a variety of application. For example the use of a very strong field ligand N,N'-dimethyl-N,N'-dipyridine-2-ylpyridine-2,6-diamine yields a water soluble near-IR luminescent Cr(III) complex, which may have application in biological imaging and sensing.[3] Recent studies have also shown that relatively simple Cr(III) complexes of 1,10-phenanthroline and 2,2'-bipyridine type ligands may have application in the design of non-volatile memory device materials.[4] Herein we report our investigations into a series of Cr(III) complexes that incorporate 8-quinolinato type ligands within the coordination sphere, including mixed ligand variants.

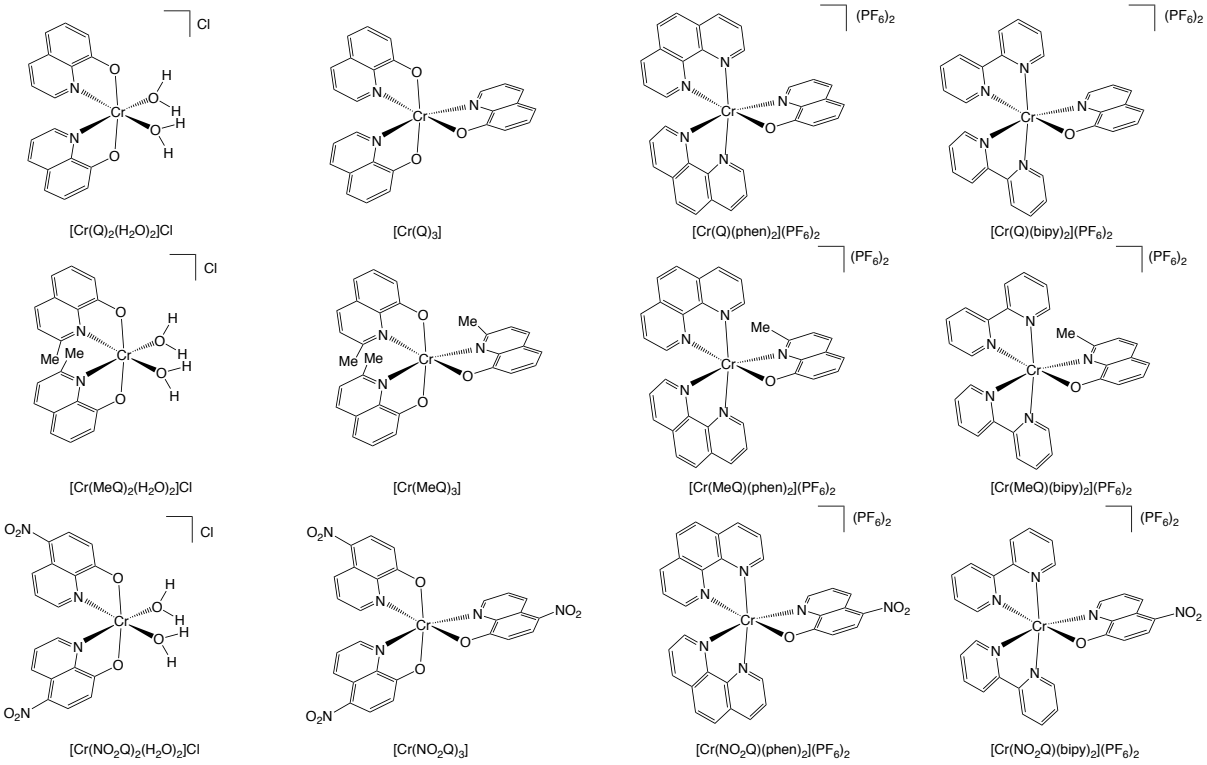
The coordination chemistry of 8-hydroxyquinoline (often referred to as 'oxine') is extremely well known and dates back many decades. Historically it has found important uses in analytical chemistry and separation techniques,[5] and luminescent coordination compounds.[6] More recent developments have included its utility in the development of supramolecular chemistry where its coordination chemistry and molecular recognition features can be exploited.[7] Further interest in 8-hydroxyquinoline has been stimulated by its use in medicinal chemistry,[8] and as a chelating species in the development of potential radioimaging agents based upon Ga-68,[9] In-111,[10] Zr-89[11] and, most recently, Mn-52.[12]

Complexes of 8-hydroxyquinoline with Cr(III) have been reported,[13] although it is only recently that the structural, spectral and electrochemical properties of $[Cr(Q)_3]$ (where Q = 8-quinolinato) have been described in detail.[14] Consequently, examples of mixed ligand systems of Cr(III) which incorporate 8-quinolinato chelates appear to be quite rare. The current study includes structural, analytical and spectroscopic characterisation of these new Cr(III) complexes, including luminescence properties.

Results and discussion

Synthesis of the complexes

Three types of Cr(III) complex (Scheme 1) were synthesised that incorporate 8-quinolinato (Q) ligands: homoleptic $[Cr(Q)_3]$, bis aquo species $[Cr(Q)_2(H_2O)_2]Cl$, and mixed ligand $[Cr(Q)(N\text{^}N)_2](PF_6)_2$ (where Q = quinolinato ligand, and N^N = 1,10-phenanthroline or 2,2'-bipyridine). $[Cr(Q)_2(H_2O)_2]Cl$ complexes were synthesised by heating $CrCl_3.6H_2O$ and two equivalents of a 8-hydroxyquinoline ligand in ethanol/H_2O to reflux for three hours; the ligand variants were 8-hydroxyquinoline (HQ), 2-methyl-8-hydroxyquinoline (MeHQ) and 5-nitro-8-hydroxyquinoline (NO_2HQ). The $[Cr(Q)_3]$ species were obtained in a similar manner using three equivalents of ligand. The heteroleptic $[Cr(Q)(N\text{^}N)_2](PF_6)_2$ complexes were synthesised by stirring the appropriate precursor species $[Cr(N\text{^}N)_2(CF_3SO_3)_2](CF_3SO_3)$ with the HQ ligand in acetonitrile at room temperature for 12 hours. Excess KPF_6 was then added to induce precipitation of the products. The yields for all complexations were between 57-80%, and air and moisture-stable solids were obtained in all cases. The complete series of synthesised complexes is represented in Scheme 1.



Scheme 1. The Cr(III) coordination complexes synthesised in this study.

X-ray crystallographic studies

All crystals were grown using vapour diffusion techniques. Data collection parameters are presented in Table 1, and all key bond lengths and bond angles that describe the coordination spheres are presented in subsequent Tables 2-5.

Table 1. Crystallographic data for compounds $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$ (**1**), $[Cr(Q)(phen)_2](PF_6)_2.MeCN$ (**2**), $[Cr(MeQ)(bipy)_2](PF_6)_2.H_2O$ (**3**) and $[Cr(NO_2Q)(bipy)_2](PF_6)_2.2MeCN$ (**4**).

Compound	**1**	**2**	**3**	**4**
Chemical Formula	$C_{20}H_{23}ClCrN_2O_{5.50}$	$C_{35}H_{25}CrF_{12}N_6OP_2$	$C_{30}H_{26}CrF_{12}N_5O_2P_2$	$C_{33}H_{27}CrF_{12}N_8O_3P_2$
Mr. g.mol^{-1}	466.85	887.55	830.50	925.56
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*–1	*P*–1	$P2_1/n$	*P*–1
T(K)	100(2)	100(2)	100(2)	100(2)
a, Å	12.0329(3)	10.3602(3)	10.0830(3)	9.7304(3)
b, Å	12.1647(3)	12.7649(3)	14.2406(3)	12.3923(5)
c, Å	14.9310(4)	14.7897(4)	23.9077(6)	17.3417(4)
α, degree	88.506(2)	101.265(2)	90°	107.519(3)°
β, degree	84.436(2)	96.942(2)	101.734(3)°	95.633(2)°
γ, degree	82.002(2)	111.499(2)	90°	109.667(3)°
Z	4	2	4	2
Dc. Mg/m^3	1.440	1.690	1.641	1.679
$\mu(M_O K \alpha)$, mm^{-1}	0.691	0.526	0.541	0.510
Reflections collected	17846	26044	37009	30575
Unique reflections	17846	7986	7707	8377
R_{int}	0	0.0209	0.0290	0.0265
R1[I>2σ<(I)]	0.0784	0.0350	0.0448	0.0626
wR2(all data)	0.1762	0.0933	0.1228	0.1821
CCDC:	1865072	1865075	1865074	1865073

Crystal structure of $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$

$[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$ crystallises in the triclinic space group *P-1.* There are 2 independent Cr(III) complexes within the asymmetric unit that are similar thus only one is described below. The Cr(III) cation lies at the centre of a slightly distorted octahedral coordination sphere. The two bidentate MeQ ligands are arranged so that the oxygen

donors are trans to one another, and the nitrogens are *cis*; the two water molecules are in a mutually *cis* arrangement (Figure 1a-c). The Cr-O41 and Cr-O42 bond lengths (Table 2) relate to the coordinated water molecules and are longer than those found for Cr-O1 and Cr-O11. The Cr-O coordinative bond lengths range from 1.923(3) to 1.986(3) Å, and the Cr-N bond lengths are significantly longer and range from 2.096(4) to 2.100(4) Å. It is typical in Cr(III) complexes coordinated by six donor atoms (2N, 2O and 2O from two H_2O molecules) that the bond length of Cr-O is shorter than Cr-N, and Cr-O shorter than Cr-OH_2: the Cr-O distances range from 1.917-1.958, and Cr-OH_2 distances range from 1.982-2.006 Å and Cr-N range from 2.030-2.067 Å.[15] The bond angles O11–Cr1–O1 and O42–Cr1–N11 are 172.45(14)º and 167.57(15)º respectively (Table 2). The pyridyl ring in each quinolinato ligand is nearly perpendicular to the other MeQ molecule (N11-Cr1-N1 91.94(15)º). Two intermolecular hydrogen bonds are observed between the hydrogen atom in the coordinated water and the chloride ion (O42–H42A···Cl1 at 2.21 Å), and between the hydrogen atom of the same coordinated water molecule and the oxygen atom in the uncoordinated water (O42–H42B···O45^{i} and the bond length is 1.72 Å). Furthermore, the uncoordinated water molecule H-bonds with the oxygen atom of the MeQ ligand (O45–H45B···O11, the bond length is 1.95 Å).

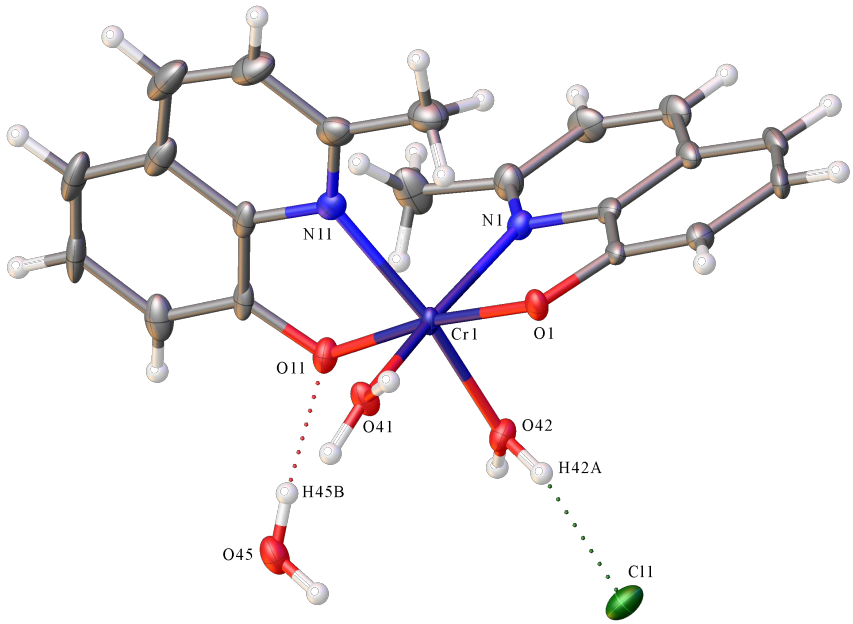


Figure 1a. Structural representation of one complex of $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$. Ellipsoids drawn at 50%.

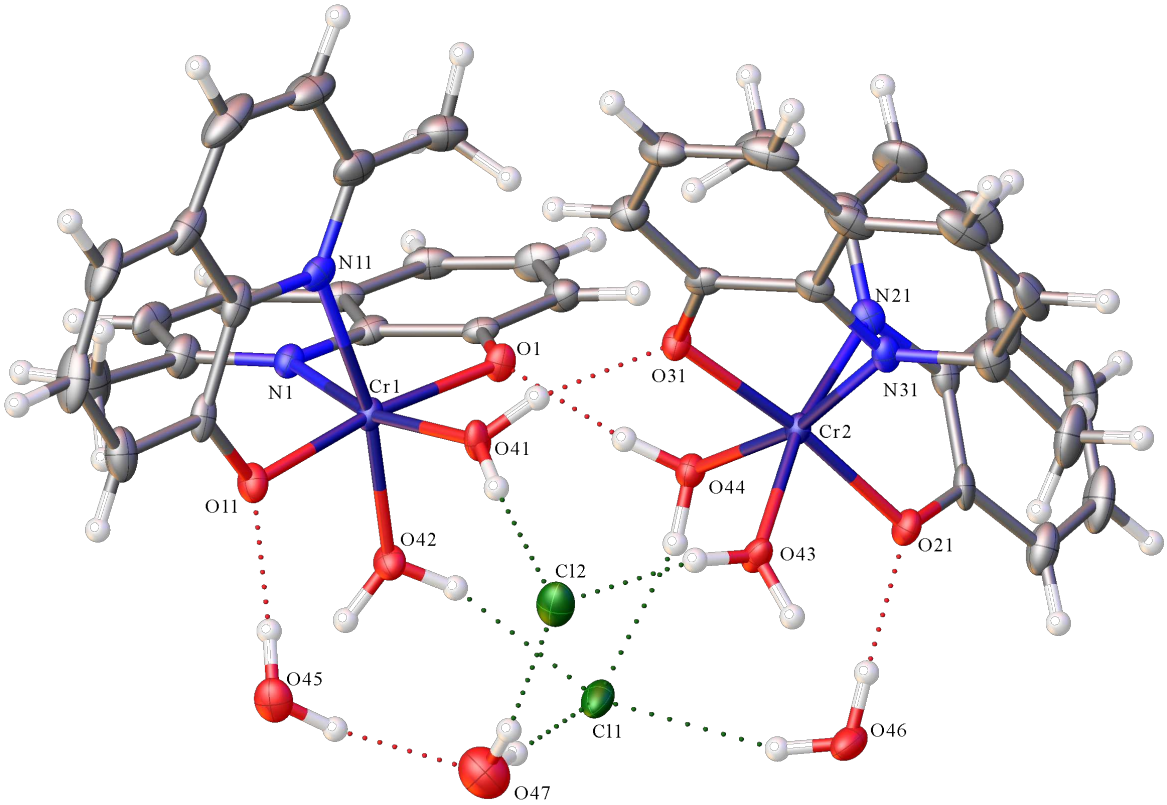


Figure 1b. Structural representation of the two complexes of $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$. Ellipsoids drawn at 50%.

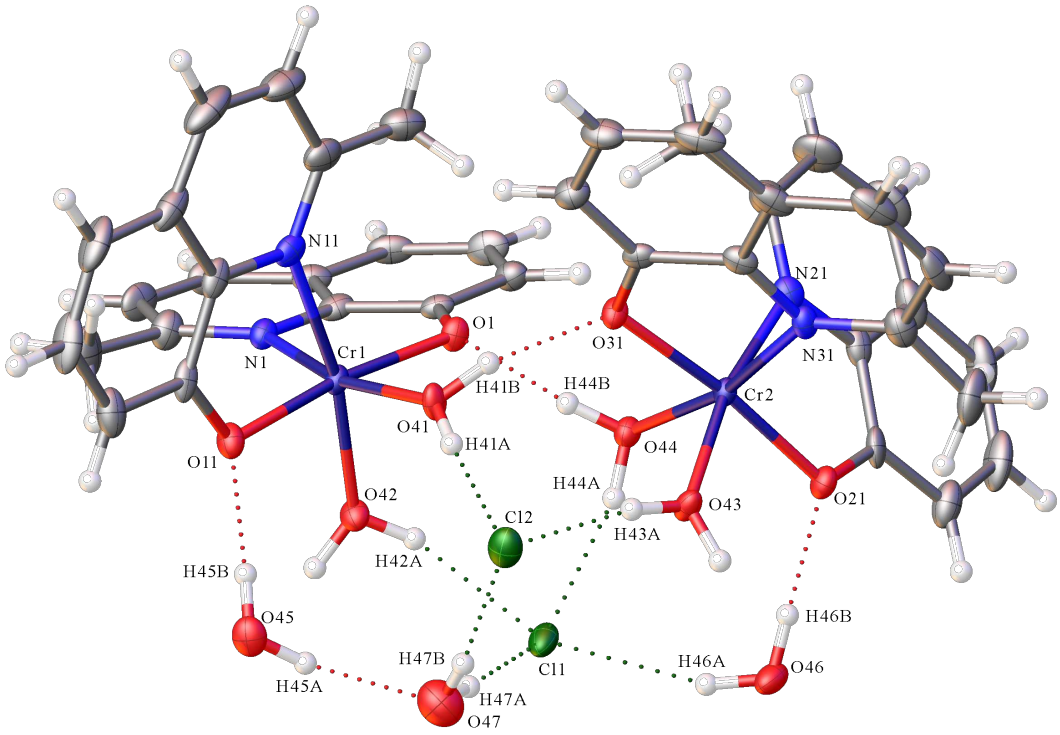


Figure 1c. Structural representation of the two complexes of $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$. Ellipsoids drawn at 50% (hydrogen bonding and hydrogen atoms labelled).

Table 2. Selected bond lengths (Å) and bond angles (º) for $[Cr(MeQ)_2(H_2O)_2]Cl$.

Bond length (Å)			
Cr1–O11	1.923(3)	Cr1–O41	1.986(3)
Cr1–O1	1.944(3)	Cr1–N11	2.096(4)
Cr1–O42	1.980(3)	Cr1–N1	2.100(4)
Cr2–O31	1.941(3)	Cr2–O43	1.978(3)
Cr2–O21	1.918(3)	Cr2–N31	2.092(4)
Cr2–O44	2.000(3)	Cr2–N21	2.109(4)
Bond Angles (º)			
O11–Cr1–O1	172.45(14)	O42–Cr1–N11	167.57(15)
O11–Cr1–O42	85.62(14)	O41–Cr1–N11	86.92(14)
O1–Cr1–O42	89.00(13)	O11–Cr1–N1	103.12(14)
O11–Cr1–O41	91.12(13)	O1–Cr1–N1	82.02(14)
O1–Cr1–O41	84.11(13)	O42–Cr1–N1	88.80(14)
O42–Cr1–O41	95.42(14)	O41–Cr1–N1	165.43(14)
O11–Cr1–N11	82.13(15)	N11–Cr1–N1	91.94(15)
O1–Cr1–N11	103.39(15)		
O31–Cr2–O21	173.57(14)	O44–Cr2–N31	167.01(14)
O31–Cr2–O44	85.69(13)	O43–Cr2–N31	91.10(14)
O21–Cr2–O44	90.34(13)	O31–Cr2–N21	102.70(15)
O31–Cr2–O43	89.79(13)	O21–Cr2–N21	82.07(15)
O21–Cr2–O43	85.42(13)	O44–Cr2–N21	86.66(14)
O44–Cr2–O43	93.66(13)	O43–Cr2–N21	167.49(15)
O31–Cr2–N31	82.25(14)	N31–Cr2–N21	91.29(15)
O21–Cr2–N31	102.10(14)		

Crystal structure of $[Cr(Q)(phen)_2](PF_6)_2.MeCN$

Red crystals of $[Cr(Q)(phen)_2](PF_6)_2$ were obtained by vapour diffusion of diethyl ether into an acetonitrile solution of the complex. The complex crystallises in the triclinic space group *P-1* and contains a single complex within the asymmetric unit (Figure 2). Based on the bond angles about the metal centre which range from 79.89(5)-99.47(5)º and 168.44(5)-175.88(5)º, the geometry of the complex is best considered as slightly distorted N_5O octahedral (Table 3). One of the PF_6^- counter ions is disordered over three positions, and one MeCN solvent of crystallization is observed in the structure. Four of the nitrogen donor atoms (N11, N12, N31 and N32) originate from the two phenanthroline molecules while the fifth and sixth coordinating atoms are the nitrogen and oxygen donor atoms, N1 and O1 from the quinolinato ligand. Relatively few Cr(III) compounds with a N_5O donor set have been crystallographically characterised,[16] but this is a rare example of quinolinato derivative to be crystallographically characterized as part of a N_5O coordination sphere around a Cr(III) centre. The Cr-N and Cr-O bond

lengths are similar to $[Cr(MeQ)_2(H_2O)_2]Cl$ and range from 2.0495(14)-2.0729(13) Å for the Cr-N bonds and is 1.9059(11) Å for the Cr-O bond.

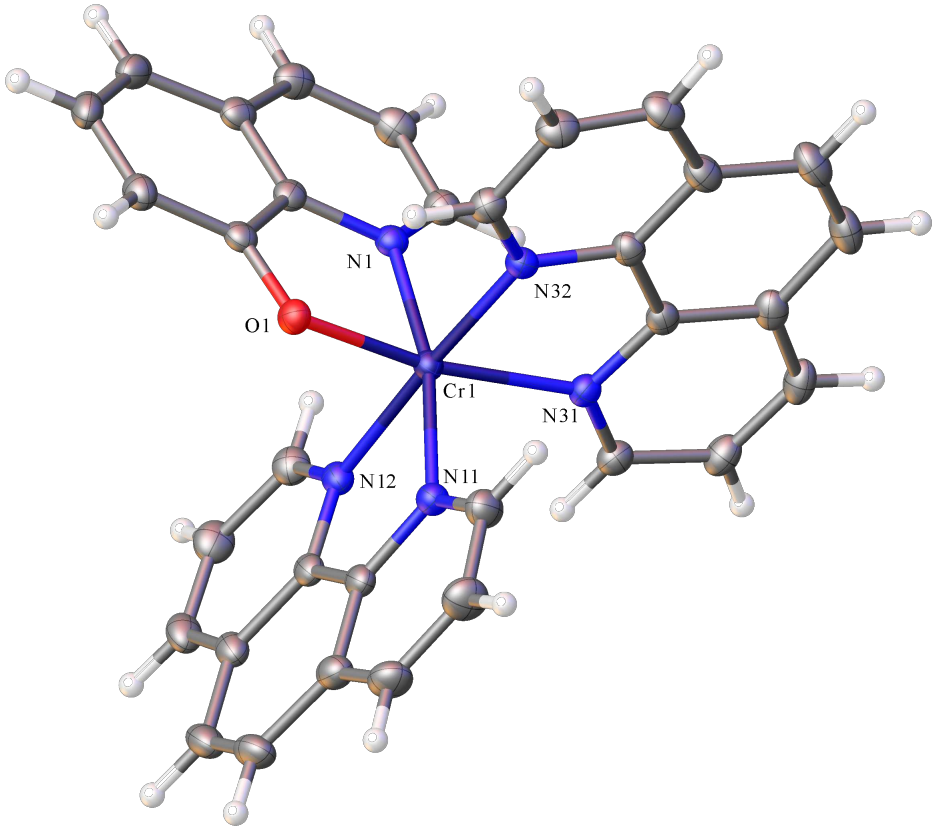


Figure 2: Structural representation of complex $[Cr(Q)(phen)_2](PF_6)_2$.MeCN. Ellipsoids drawn at 50% (PF_6 anions and solvent MeCN omitted).

Table 3. Selected bond lengths (Å) and bond angles (º) for $[Cr(Q)(phen)_2](PF_6)_2$.

Bond length (Å)			
Cr1–O1	1.9059(11)	Cr1–N32	2.0497(13)
Cr1–N1	2.0475(13)	Cr1–N12	2.0701(14)
Cr1–N11	2.0495(14)	Cr1–N31	2.0729(13)
Bond Angles (º)			
O1–Cr1–N1	83.20(5)	N11–Cr1–N12	80.64(5)
O1–Cr1–N11	89.18(5)	N32–Cr1–N12	175.88(5)
N1–Cr1–N11	168.44(7)	O1–Cr1–N31	169.85(5)
O1–Cr1–N32	91.20(5)	N1–Cr1–N31	92.43(5)
N1–Cr1–N32	93.48(5)	N11–Cr1–N31	96.44(5)
N11–Cr1–N32	95.37(5)	N32–Cr1–N31	79.89(5)
O1–Cr1–N12	89.76(5)	N12–Cr1–N31	99.47(5)
N1–Cr1–N12	90.62(5)		

Crystal structures of $[Cr(MeQ)(bipy)_2](PF_6)_2.H_2O$ and $[Cr(NO_2Q)(bipy)_2](PF_6)_2.2$ MeCN

Red crystals of $[Cr(MeQ)(bipy)_2](PF_6)_2$ were obtained by vapour diffusion of diethyl ether into an acetonitrile solution of the complex. The complex crystallises in the monoclinic space group $P2_1/n$ and contains a single complex and one water molecule of crystallization within the asymmetric unit (Figure 3). Similar to $[Cr(Q)(phen)_2](PF_6)_2$, the Cr(III) ion is surrounded by five nitrogen and one oxygen atoms within the coordination sphere, with two PF_6^- counter ions within the lattice framework. The two bipyridine ligands coordinate through N11, N12, N21 and N22 while the fifth and sixth coordinating atoms are N1 and O1 from MeQ ligand. Again, $[Cr(MeQ)(bipy)_2](PF_6)_2$ shows a slightly distorted octahedral geometry which is very similar to $[Cr(Q)(phen)_2](PF_6)_2$.

$[Cr(NO_2Q)(bipy)_2](PF_6)_2$ crystallises in the *P*-1 space group and the structure reveals two MeCN solvent molecules of crystallization. One of the PF_6^- counter ions is disordered. The structure is analogous to $[Cr(MeQ)(bipy)_2](PF_6)_2$ with only very minor deviations in the bond lengths describing the coordination sphere. These observations suggest that the nature of the substituent on the quinolinato ligand (electron donating methyl *versus* electron withdrawing nitro) has little influence upon the strength of the metal ligand bonding.

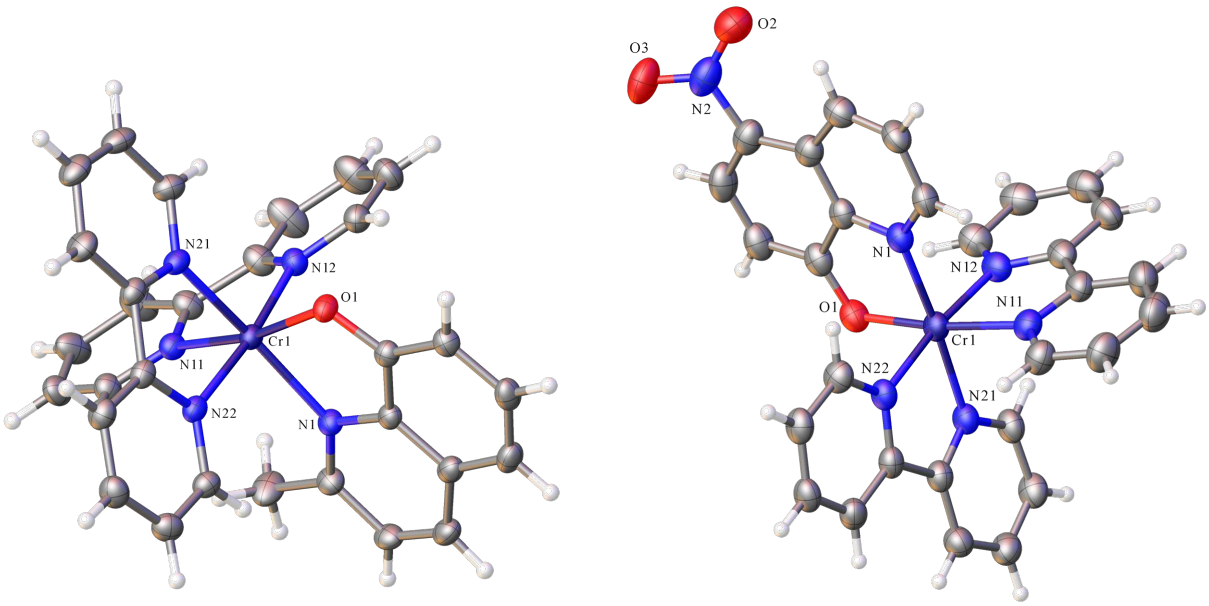


Figure 3. Structural representations of complex $[Cr(MeQ)(bipy)_2](PF_6)_2$ (left) and $[Cr(NO_2Q)(bipy)_2](PF_6)_2$. Ellipsoids drawn at 50% (PF_6 anions and solvent omitted).

Table 4. Selected bond lengths (Å) and bond angles (º) for $[Cr(MeQ)(bipy)_2](PF_6)_2$.

Bond length (Å)			
Cr1–O1	1.9084(15)	Cr1–N22	2.0794(18)
Cr1–N21	2.0533(18)	Cr1–N11	2.0822(18)
Cr1–N12	2.0626(19)	Cr1–N1	2.0916(18)
Bond Angles (º)			
O1–Cr1–N21	88.36(7)	N12–Cr1–N11	78.16(8)
O1–Cr1–N12	92.25(7)	N22–Cr1–N11	96.23(7)
N21–Cr1–N12	96.71(7)	O1–Cr1–N1	83.22(7)
O1–Cr1–N22	92.94(7)	N21–Cr1–N1	166.78(7)
N21–Cr1–N22	79.26(7)	N12–Cr1–N1	93.80(7)
N12–Cr1–N22	173.33(7)	N22–Cr1–N1	90.97(7)
O1–Cr1–N11	168.82(7)	N11–Cr1–N1	102.95(7)
N21–Cr1–N11	87.08(7)		

Table 4: Selected bond lengths (Å) and bond angles (º) for $[Cr(NO_2Q)(bipy)_2](PF_6)_2$.

Bond length (Å)			
Cr1–O1	1.917(2)	Cr1–N12	2.046(3)
Cr1–N1	2.039(2)	Cr1–N21	2.048(3)
Cr1–N22	2.048(2)	Cr1–N11	2.062(3)
Bond Angles (º)			
O1–Cr1–N1	82.23(10)	N22–Cr1–N12	173.38(10)
O1–Cr1–N22	89.70(10)	N22–Cr1–N21	79.46(10)
N1–Cr1–N22	97.17(10)	O1–Cr1–N21	95.42(10)
O1–Cr1–N12	94.22(10)	N1–Cr1–N21	175.93(10)
N1–Cr1–N12	88.65(10)	N12–Cr1–N21	94.84(10)
N12–Cr1–N11	79.03(11)	N22–Cr1–N11	97.39(10)
O1–Cr1–N11	172.23(10)	N11–Cr1–N1	93.69(10)
N21–Cr1–N11	89.03(10)		

General characterisation of the Cr(III) complexes

A range of analytical and spectroscopic techniques were used to characterize the complexes. IR spectra of the Cr(III) complexes were recorded over the range 4000–400 cm^{-1} and selected bands are presented in the experimental section and confirm the presence of the ligand in each case. The IR spectra of the bis aquo Cr(III) complexes show the presence of O-H vibrations which are attributed to the hygroscopic nature of these species and the coordinated water molecules. The spectra for the $[Cr(Q)(N\hat{}N)_2](PF_6)_2$ complexes also showed the presence of the

hexafluorophosphate counter anion ca. 835 cm^{-1}. Mass spectrometry data was obtained for all complexes generally showing the parent ion or a cationic fragment with isotopic distributions consistent with the presence of chromium. Satisfactory elemental analyses were obtained for each complex, with the bis aquo complexes, in particular, showing the presence of additional water. This reflects the likely hygroscopic nature of these complexes and is consistent with the IR data and crystal structure of $[Cr(MeQ)_2(H_2O)_2]Cl.3/2H_2O$.

Electrochemical studies

The electrochemical data for the Cr(III) complexes were obtained in acetonitrile using $[Bu_4N][PF_6]$ (0.1 M) as the supporting electrolyte. The data is tabulated for all Cr(III) complexes in Table 5 and focused upon the reduction processes (no oxidative processes were clearly observed in the solvent window). The cyclic voltammograms of these complexes are very similar, showing two reduction processes in the regions -1.34 to -1.66 V and -1.91 to -2.17 V (*versus* Fc/Fc^+). The first of these reductions was deduced to be reversible with peak to peak separations 59-72 mV. Furthermore, the ratio of i_{pc} to i_{pa} is ~1 supporting the reversible nature of these processes. From the data, the reduction potentials for the NO_2Q derivatives were more positive relative to the unsubstituted analogues; the methyl-substituted complexes were at more negative potentials. This pattern is consistent with the anticipated electron donating or withdrawing capacities of these different substituents. Monzon *et al.* have investigated the electrochemical potentials for $[Cr(Q)_3]$ and reported two reversible peaks at -1.54 and -2.03 V (*vs* Fc/Fc^+) which they attribute to the Cr(III)/Cr(II) couple and the quinolinato ligand system, respectively.[17] Our own measurements compare favorably with those reported, and the other complexes in the series follow a similar pattern. Therefore the first reduction potential at -1.34 to -1.66 V may be due to a metal-centred process (forming low spin Cr(II).[18] The second potential at -1.91 to -2.17 V is attributed to a ligand-centred reduction although it is unclear for the mixed ligand complexes whether this can attributed solely to the quinolinato ligands.

Electronic properties of the complexes

The magnetic moments (μ_{eff}) of the Cr(III) complexes were measured using the Evans' method[19] in DMSO solvent at room temperature. The obtained values of 3.73-4.08 B.M. (see Experimental section) are consistent with the d^3 configuration of Cr(III).

The electronic spectra of the Cr(III) complexes were measured in DMF solutions and their spectral data are tabulated in Table 5. Taking the tris quinolinate complex $[Cr(Q)_3]$ as a reference, the spectrum displayed the expected bands that have been noted previously.[20] Thus, ligand centred bands were noted at 319 and 413 nm, each being attributed to transitions with $\pi \rightarrow \pi^*$ character. The 413 nm band was bathochromically shifted relative to free 8-hydroxyquinoline. In addition to these bands, a much weaker intensity longer wavelength band, often visible as a shoulder feature in these complexes, was noted at approximately 546 nm ($\varepsilon \approx 100\ M^{-1}cm^{-1}$) and assigned to the metal-centred *d-d* transition $^4A_2 \rightarrow {}^4T_2$, again in broad agreement with previous work.[21]

Replacing one of the 8-quinolinato ligands with two water molecules ($[Cr(Q)_2(H_2O)_2]Cl$) resulted in comparable ligand centred transitions and a general lowering of the $^4A_2 \rightarrow {}^4T_2$ transition energy, the latter probably reflecting the overall weakening of the ligand field at Cr(III). The remaining mixed ligand $[Cr(Q)(N\hat{}N)_2](PF_6)_2$ complexes again showed similar spectral features, but with additional contributions at higher energy that can be assigned to the $\pi \rightarrow \pi^*$ transitions within the bipy/phen ligands. This is consistent with the numerous reports on polypyridine complexes of Cr(III).[22] It should also be noted that in Cr(III) polypyridyl complexes, ligand-to-metal charge transfer (LMCT) bands are also known to contribute in the UV region. Again, for $[Cr(Q)(N\hat{}N)_2](PF_6)_2$ the weak $^4A_2 \rightarrow {}^4T_2$ transition was observable between 507-545 nm in all cases, with the highest energy noted for $[Cr(Q)(phen)_2](PF_6)_2$ which is consistent with a strong ligand field at Cr(III).

Table 5: Electronic properties of the Cr(III) complexes in solution.

Complex	Absorption, λ_{max} / nm [a]		Emission, λ_{em} / nm[b]	Reduction potentials, $E_{1/2}$ / V[c]	
	$\pi \rightarrow \pi^*$	*d-d*			
$[Cr(Q)_3]$	319, 413	546	500	-1.56	-2.07
$[Cr(MeQ)_3]$	308, 404	579	511	-1.66	-2.17
$[Cr(NO_2Q)_3]$	333, 408	529	476	-1.42	-1.95
$[Cr(Q)_2(H_2O)_2]Cl$	315, 403	565	495	-1.48	-2.02
$[Cr(MeQ)_2(H_2O)_2]Cl$	291, 402	563	504	-1.64	-2.14
$[Cr(NO_2Q)_2(H_2O)_2]Cl$	332, 427	594	463	-1.39	-1.92
$[Cr(Q)(phen)_2](PF_6)_2$	273, 366	507	500	-1.46	-2.06
$[Cr(MeQ)(phen)_2](PF_6)_2$	276, 374	515	507	-1.57	-2.12
$[Cr(NO_2Q)(phen)_2](PF_6)_2$	271, 385	531	492	-1.34	-1.91
$[Cr(Q)(bipy)_2](PF_6)_2$	304, 386	545	484	-1.43	-2.02
$[Cr(MeQ)(bipy)_2](PF_6)_2$	305, 441	533	493	-1.57	-2.10
$[Cr(NO_2Q)(bipy)_2](PF_6)_2$	306, 399	533	472 (vw)	-1.37	-1.93

[a] DMF solution; [b] aerated MeCN solution; [c] deoxygenated MeCN solution, 0.1 M $[Bu_4N][PF_6]$ supporting electrolyte, measured at 100 mV/s. Potential versus Fc/Fc^+.

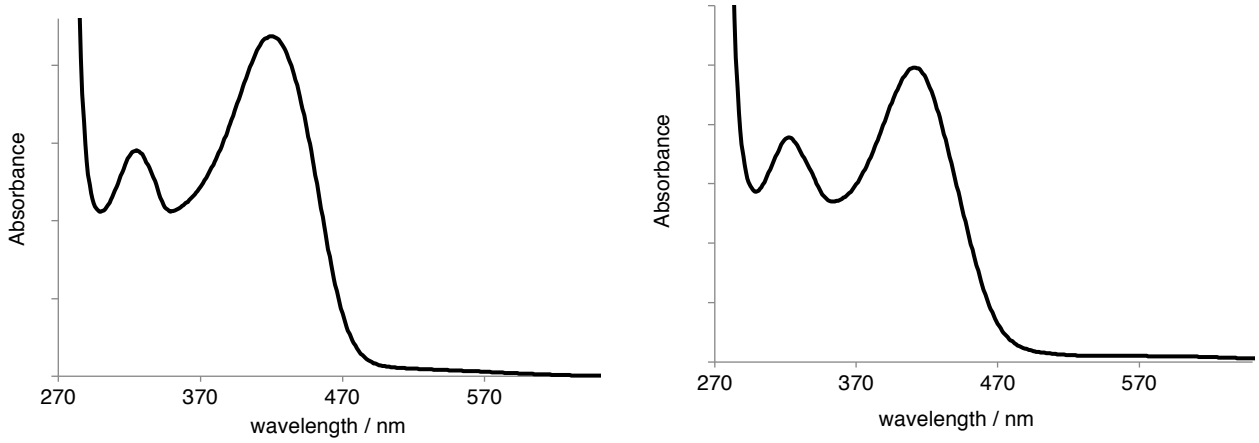


Figure 4. Absorption spectra of $[Cr(Q)_3]$ (left) and $[Cr(Q)_2(H_2O)_2]Cl$ (right).

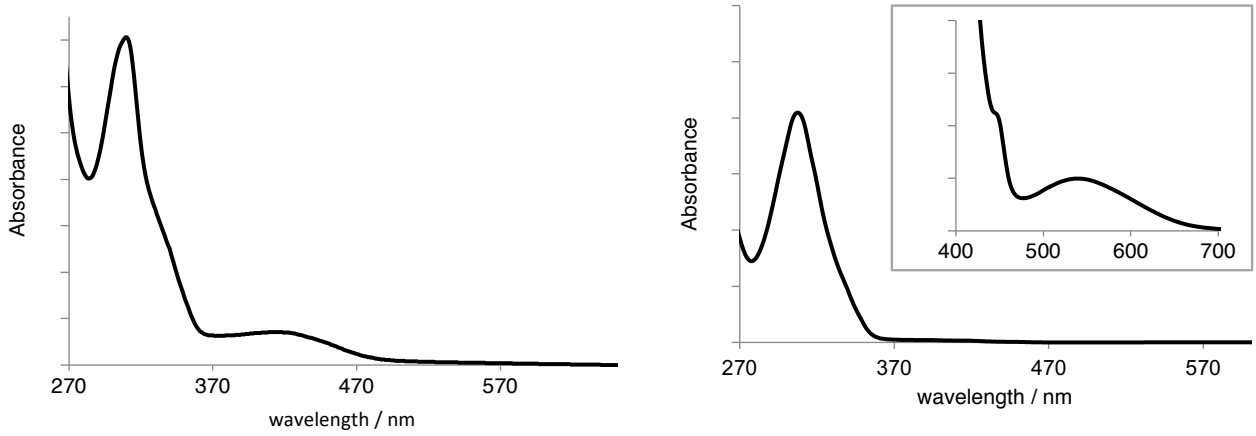


Figure 5. Absorption spectra of $[Cr(Q)(bipy)_2](PF_6)_2$ (left) and $[Cr(MeQ)(bipy)_2](PF_6)_2$ (right) with $^4A_2 \rightarrow {}^4T_2$ transition shown (inset).

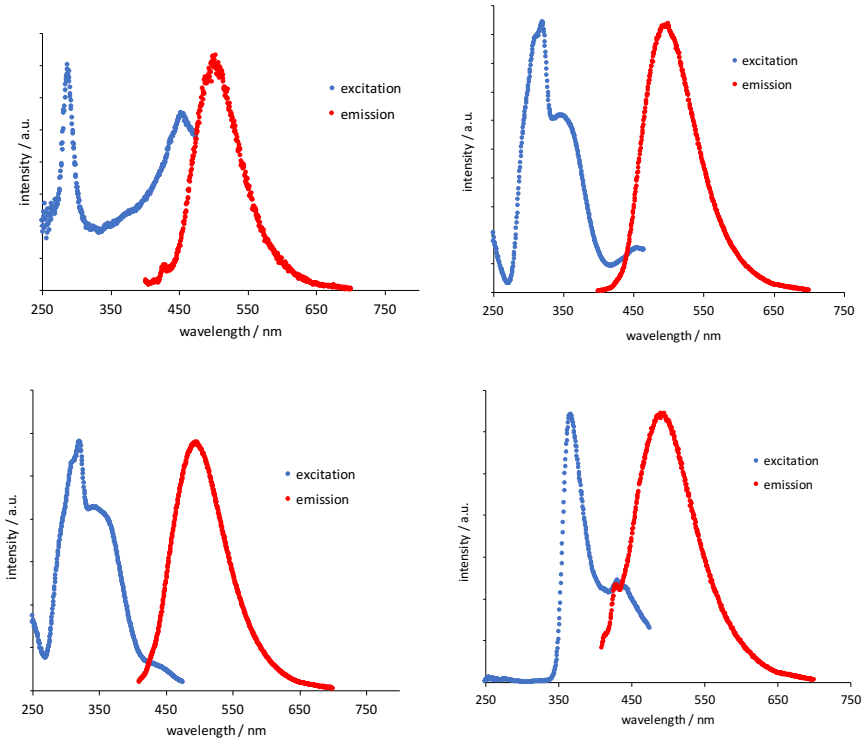


Figure 6. Steady state emission (red) and excitation (blue) spectra (MeCN) for $[Cr(Q)_3]$ (top left), $[Cr(MeQ)_3]$ (top right), $[Cr(MeQ)_2(H_2O)_2]Cl$ (bottom left) and $[Cr(MeQ)(bipy)_2](PF_6)_2$ (bottom right).

Luminescence studies of the complexes were undertaken on aerated MeCN solutions at room temperature (Figure 6). Previous studies have described $[Cr(Q)_3]$ as non-

luminescent or very weakly emissive at room temperature.[20] However, in solution following irradiation at 380 nm, which corresponds to excitation of the ligand-centred transitions, we observed an emission band at 500 nm (Figure 6). This recorded emission wavelength for $[Cr(Q)_3]$ compares quite well to the green fluorescence character often attributed to oxine complexes of Al(III)[23] and Zn(II).[24]

Substituting the quinolinato ligand subtly modulated these spectral features, presumably due to the change in the electronics of the coordinated ligand. For example, $[Cr(NO_2Q)_3]$ gave a hypsochromic shift in the emission band to 476 nm. The related bis aquo complexes retained the luminescence character, with emission in the range 463-504 nm which is again indicative of a quinolinato-centred fluorescence. The appearance of the excitation spectra for these species was very closely related to the tris-quinolinato species (Figure 6). Further solvent studies on the bis aquo complexes showed that the emission character was retained in aqueous solution.

Finally, for the $[Cr(Q)(N\text{^}N)_2](PF_6)_2$ complexes, similar luminescence properties were again observed with a broad peak around 500 nm, and thus comparable to the other complexes in this study. These species produced markedly different excitation spectra with a much more intense peak at shorter wavelengths (*ca*. 365 nm), which may relate to transitions within the coordinated diimine ligands. For these Cr(III) complexes, there was no evidence of any metal-centred phosphorescence peaks in the typical range 700-800 nm at room temperature.[25]

Conclusion

8-hydroxyquinoline complexes of Cr(III) can be prepared to give six coordinate homoleptic or heteroleptic species. In all cases the complexes are highly coloured and demonstrated luminescence in the visible region, which was attributed to ligand-centred excited states. The electronic properties can be subtly modulated through substituents on the 8-quinolinato ligand; these observations were further supported by electrochemical properties. Four structural examples were determined with X-ray data revealing octahedral species in each case. For the bis aquo complex the structure confirmed the mutually *cis* arrangement of the coordinated water molecules.

Experimental

General Experimental Considerations

All reagents and solvents were commercially available and were used without further purification if not stated otherwise. Petroleum ether refers to the 40-60 °C fraction. Low-resolution mass spectra were obtained by the staff at Cardiff University. High-resolution mass spectra were carried out at the EPSRC National Mass Spectrometry Facility at Swansea University. High resolution mass spectral (HRMS) data were obtained on a Waters MALDI-TOF mx at Cardiff University or on a Thermo Scientific LTQ Orbitrap XL by the EPSRC UK National Mass Spectrometry Facility at Swansea University. IR spectra were obtained from a Shimadzu IR-Affinity-1S FTIR and melting points using a Gallenkamp apparatus and are reported uncorrected. Reference to spectroscopic data are given for known compounds. UV-Vis studies were performed on a Jasco V-570 spectrophotometer as MeCN solutions (2.5 or 5 × 10^{-5} M). Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module as MeCN solutions. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 459 nm output operating at 1 MHz. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software.

X-ray Diffraction

For the four samples (for reference see Table 1), a suitable crystal[26] was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ (45.0 kV, 55.0 mA) equipped with either VHF Varimax confocal mirrors (70μm focus) (**2**, **3**) or HF Varimax confocal mirrors (100μm focus) (**1**, **4**) and an AFC12 goniometer with HG Saturn 724+ detector ([HL^3]PF_6). The crystals were kept at T = 100(2) K during data collection. Data were measured using profile data from ω-scans using MoK_α radiation. Cell determination and data collection were carried out using CrystalClear[27], with the data reduction, cell refinement and absorption correction using CrystalisPro[28].CrystalisPro. Using Olex2[29], the structures were solved with the ShelXT[30] structure solution program and the

models were refined with version 2018/3 of ShelXL [31] using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. **1** was solved as a non-merohedral twin (62:38) with 180° rotation about direct axis (0.71 - 0.70 0). The other samples each have a disordered PF_6 anion resulting in the use of geometrical (SADI) and displacement (RIGU) restraints (**3** also has a disordered water molecule).

CCDC1865072-1865075 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [Cr(Q)$_3$]

The general method was to use a solution of $CrCl_3.6H_2O$ (1 eq.) in 5 cm^3 water which was poured into the solution of the appropriate 8-hydroxyquinoline (either 2 or 3 eq.) in 15 cm^3 ethanol. The mixture was heated to reflux for 3 hours. The solution then changed from green to brown. After this time, the mixture solution was concentrated to 5 ml. The formed precipitate was filtered, washed with acetone 20 cm^3 and ether 10 cm^3 and then dried under vacuum. For **[Cr(Q)$_3$]**, 8-hydroxyquinoline (0.83 g, 5.7 mmol) and $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) were used giving the product as a green powder. Yield: 0.87 g, 80%. ESI-MS (*m/z*): 484.08 [M^+]; HRMS found *m/z* 484.0754, calc. mass: 484.0753. Selected FT-IR (cm^{-1}): ν(C=N) 1570, ν(C-O) 1110. UV-vis. λ_{max} (εM, $M^{-1}cm^{-1}$): 319 (5400), 413 (3500) and 546 (110) nm. Elemental Analysis: calcd. for $C_{27}H_{18}CrN_3O_3.CH_3CH_2OH$ (%): C, 65.66; H, 4.56; N, 7.92; found (%): C, 65.25; H, 4.88; N, 7.96. Magnetic moment μ_{obs} (B.M.): 3.863.

Synthesis of [Cr(MeQ)$_3$]

Using 8-hydroxy-2-methylquinoline (0.91 g, 5.7 mmol) and $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) giving the product as a green powder. Yield: 0.95 g, 80%. ESI-MS (*m/z*): 526.12 [M^+]; HRMS found *m/z* 526.1223, calc. mass: 526.1223. Selected FT-IR (cm^{-1}): ν(C=N) 1550, ν(C-O) 1107. UV-vis., λ_{max} (ε, $M^{-1}cm^{-1}$): 308 (3900), 404 (2500) and 579

(40) nm. Elemental analysis. calcd. for $C_{30}H_{24}CrN_3O_3.3H_2O$ (%): C, 62.06; H, 5.21; N, 7.24; found (%): C, 62.41; H, 5.05; N, 7.50. Magnetic moment μ_{obs} (B.M.): 3.731.

Synthesis of $[Cr(NO_2Q)_3]$

Using 8-hydroxy-5-nitroquinoline (1.08 g, 5.7 mmol) and $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) giving the product as a brown powder. Yield: 1.05 g, 74%. ESI-MS (*m/z*): 618.95 [M^+]; HRMS found *m/z* 619.0296; calc. mass 619.0306. Selected FT-IR (cm^{-1}): ν(C=N) 1570, ν(C-O) 1099. UV-vis., λ_{max} (ε, $M^{-1}cm^{-1}$): 333 (7300), 408 (2300) and 529 (390) nm. Elemental analysis: calcd. for $C_{27}H_{15}CrN_6O_9$ (%): C, 52.35; H, 2.44; N,13.57; found (%): C, 52.28; H, 2.57; N, 13.49. Magnetic moment μ_{obs} (B.M.): 3.825.

Synthesis of $[Cr(Q)_2(H_2O)_2]Cl$

Using $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) and 8-hydroxyquinoline (0.545 g, 3.8 mmol) giving a brown powder. Yield (0.38 g, 71 %). ESI-MS *(m/z)*: 376.06 [M^+]; HRMS found *m/z* 376.0753; calc. 376.0761. Selected FT-IR (cm^{-1}): ν(O-H) 3420, ν(O-H) 1377, ν(C=N) 1554, ν(C-O) 1109. UV-vis., λ_{max} (ε, M^{-1} cm^{-1}): 315 (2400), 403 (1800) and 565 (80) nm. Elemental analysis: calcd. for $C_{18}H_{16}ClCrN_2O_4.2H_2O$ (%): C,48.28; H, 4.50; N, 6.26; found (%): C, 48.95; H, 4.86; N, 6.39. Magnetic moment μ_{obs} (B.M.): 3.785.

Synthesis of $[Cr(MeQ)_2(H_2O)_2]Cl$

Using 8-hydroxy-2-methylquinoline (0.6 g, 3.8 mmol) and $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) giving the product as dark green crystals. Yield: 0.41 g, 69%. ESI-MS (*m/z*): 404.08 [M^+]; HRMS found *m/z* 404.0903; calc. mass: 404.0884. Selected FT-IR (cm^{-1}): ν(O-H) 3428, ν(O-H) 1369, ν(C=N) 1541, ν(C-O) 1105. UV-vis., λ_{max} (ε, M^{-1} cm^{-1}): 291 (1300), 402 (470) and 563 (40) nm. $C_{20}H_{20}ClCrN_2O_4.H_2O.CH_3CH_2OH$ (%): C, 52.44; H, 5.60; N, 5.56; found (%): C, 53.04; H, 6.03; N, 5.68. Magnetic moment μ_{obs} (B.M.): 3.839.

Synthesis of $[Cr(NO_2Q)_2(H_2O)_2]Cl$

Using 8-hydroxy-5-nitroquinoline (0.71 g, 3.8 mmol) and $CrCl_3.6H_2O$ (0.5 g, 1.9 mmol) giving the product as a brown powder. Yield: 0.56 g, 79%. ESI-MS (*m/z*): 504.00 [$M+K^+$]. Selected FT-IR (cm^{-1}): ν(O-H) 3437, ν(O-H) 1380, ν(C=N) 1566, ν(C-O) 1101. UV-vis., λ_{max} (ε, M^{-1} cm^{-1}): 332 (3200), 427 (1700) and 594 (120) nm. Elemental

analysis: calcd. for: $C_{18}H_{14}ClCrN_4O_8$ (%): C, 43.09; H, 2.81; N, 11.17; found (%): C, 43.29; H, 3.15; N, 11.25. Magnetic moment μ_{obs} (B.M.): 3.813.

Synthesis of $[Cr(Q)(phen)_2](PF_6)_2$

The starting material $[Cr(phen)_2Cl_2]Cl$ and $[Cr(phen)_2(CF_3SO_3)_2](CF_3SO_3)$ was prepared as described previously.[27] $[Cr(Q)(phen)_2](PF_6)_2$ was prepared by stirring at room temperature, the mixture solution of $[Cr(phen)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.58 mmol) in 10 cm^3 MeCN and 8-hydroxyquinoline (0.085 g, 0.58 mmol) in 5 cm^3 MeCN for 3 hours. Concentration of the dark red solution to 5 cm^3, and then addition of KPF_6 (0.42 g, 2.3 mmol) in 2 cm^3 H_2O resulted in a brown precipitate which was stirrer for 30 minutes. The brown precipitate was filtered, washed with 3 cm^3 H_2O and 2 cm^3 MeCN and then dried under vacuum. Red crystals of $[Cr(Q)(phen)_2](PF_6)_2$ were obtained by vapor diffusion of diethyl ether into MeCN solution of the complex. Yield: 0.32 g, 64%. ESI-MS (*m/z*): 578.03 [$M+Na^+$]. Selected FT-IR (cm^{-1}): ν(C=N) 1564, ν(C-O) 1107, ν(PF_6^-) 829. UV-vis., λ_{max} (ε, M^{-1} cm^{-1}): 273 (2700), 366 (1300) and 507(40) nm. Elemental analysis: calcd. for $C_{33}H_{22}CrF_{12}N_5OP_2.4H_2O$ (%): C, 43.15; H, 3.29; N, 7.62; found (%): C, 43.05; H, 2.86; N, 7.49. Magnetic moment μ_{obs} (B.M.): 4.038.

Synthesis of $[Cr(MeQ)(phen)_2](PF_6)_2$

As for $[Cr(Q)(phen)_2](PF_6)_2$ but using $[Cr(phen)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.58 mmol), 8-hydroxy-2-methylquinoline (0.093 g, 0.58 mmol) and KPF_6 (0.42 g, 2.3 mmol). Product was isolated as a brown powder. Yield: 0.34 g, 68%. ESI-MS (*m/z*): 570.87 [M^+]. Selected FT-IR (cm^{-1}): ν(C=N) 1558, ν(C-O) 1104, ν(PF_6^-) 830. UV-vis. λ_{max} (ε, M^{-1} cm^{-1}): 276 (3400), 374 (1800) and 515 (45) nm. Elemental analysis: calcd. for $C_{34}H_{24}CrF_{12}N_5OP_2$ (%): C, 47.46; H, 2.81; N, 8.14; found (%): C, 47.59; H, 2.98; N, 8.05. Magnetic moment μ_{obs} (B.M.): 3.968.

Synthesis of $Cr(NO_2Q)(phen)_2](PF_6)_2$

Using $[Cr(phen)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.58 mmol), 8-hydroxy-5-nitroquinoline (0.11 g, 0.58 mmol) and KPF_6 (0.42 g, 2.3 mmol). Product was isolated as a brown solid. Yield: 0.3 g, 61%. ESI-MS (*m/z*): 601.03 [M^+]; HRMS found *m/z* 601.0277; calc. mass: 601.0302. Selected FT-IR (cm^{-1}): ν(C=N) 1581, ν(C-O) 1116, ν(PF_6^-) 832. UV-vis. λ_{max} (ε, M^{-1} cm^{-1}): 271 (2400), 385 (1700) and 531 (80) nm. Elemental analysis:

calcd. for $C_{33}H_{21}CrF_{12}N_6O_3P_2$ (%): C, 44.46; H, 2.37; N, 9.43; found (%): C, 44.58; H, 2.47; N, 9.61. Magnetic moment μ_{obs} (B.M.): 4.075.

Synthesis of $[Cr(Q)(bipy)_2](PF_6)_2$

The precursor materials $[Cr(bpy)_2Cl_2]Cl$ and $[Cr(bpy)_2(CF_3SO_3)_2](CF_3SO_3)$ were prepared as described previously. $[Cr(Q)(bipy)_2](PF_6)_2$ was prepared by stirring at room temperature, the solution of $[Cr(bpy)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.62 mmol) in 10 cm^3 MeCN and 8-hydroxyquinoline (0.089 g, 0.62 mmol) in 5 cm^3 MeCN for 3 hours. Concentration of the dark red solution to 5 cm^3, and then addition of KPF_6 (0.45 g, 2.46 mmol) in 2 cm^3 H_2O gave a brown precipitate that was filtered, washed with 3 cm^3 H_2O and 2 cm^3 MeCN and then dried under vacuum to give a brown powder. Yield: 0.4 g, 80%. ESI-MS (*m/z*): 508.15 [M^+]. Selected FT-IR (cm^{-1}): ν(C=N) 1565, ν(C-O) 1115, ν(PF_6-) 833; UV-vis. λ_{max} (ε, M^{-1} cm^{-1}): 304 (8400), 386 (810) and 545(131) nm. Elemental analysis: calcd. for $C_{29}H_{22}CrF_{12}N_5OP_2.4H_2O$ (%): C,40.01; H, 3.47; N, 8.05; found (%): C, 40.59; H, 3.67; N, 8.17. Magnetic moment μ_{obs} (B.M.): 4.000.

Synthesis of $[Cr(MeQ)(bipy)_2](PF_6)_2$

Using $[Cr(bpy)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.62 mmol), 8-hydroxy-2-methylquinoline (0.1 g, 0.62 mmol) and KPF_6 (0.45 g, 2.46 mmol). Red crystals of $[Cr(MeQ)(bipy)_2](PF_6)_2$ were obtained by vapour diffusion of diethyl ether into a concentrated MeCN solution of the complex. Yield: 0.33 g, 67%. ESI-MS (*m/z*): 545.13 [$M+Na^+$]. Selected FT-IR (cm^{-1}): ν(C=N) 1560, ν(C-O) 1109, ν(PF_6^-) 835. UV-vis. λ_{max} (ε, M^{-1} cm^{-1}): 305 (4000), 441 (120) and 533 (50) nm. Elemental analysis: calcd. for $C_{30}H_{24}CrF_{12}N_5OP_2$ (%): C, 44.35; H, 2.98; N, 8.62; found (%): C, 44.49; H, 3.10; N, 8.84. Magnetic moment μ_{obs} (B.M.): 3.928.

Synthesis of $[Cr(NO_2Q)(bipy)_2](PF_6)_2$

Using $[Cr(bpy)_2(CF_3SO_3)_2](CF_3SO_3)$ (0.5 g, 0.62 mmol), 8-hydroxy-5-nitroquinoline (0.12 g, 0.62 mmol) and KPF_6 (0.46 g, 2.48 mmol). Red crystals of **$[Cr(NO_2Q)(bipy)_2](PF_6)_2$** were obtained by vapour diffusion of diethyl ether into a concentrated MeCN solution of the complex. Yield: 0.29 g, 57%. ESI-MS (*m/z*): 553.03

[M^+]; HRMS found *m/z* 554.1350; calc. mass: 554.1367. Selected FT-IR (cm^{-1}): ν(C=N) 1575, ν(C-O) 1120, ν(PF_6^-) 837. UV-vis. λ_{max} (ε, M^{-1} cm^{-1}): 306 (1950), 399 (980) and 533 (110). Elemental analysis: calcd. for $C_{29}H_{21}CrF_{12}N_6O_3P_2.2H_2O$ (%): C, 39.61; H, 2.87; N, 9.56; found (%): C, 40.22; H, 3.23; N, 9.73. Magnetic moment μ_{obs} (B.M.): 3.890.

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